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(71) Applicant: ENICHEM SYNTHESIS S.p.A.
Via Ruggero Settimo 55
I-90139 Palermo(IT)

(72) Inventor: Malatesta, Vincenzo, Dr.
21, Via Repubblica
I-20093 Cologno Monzese, Milan(IT)
Inventor: Allegrini, Pietro, Dr.
34, Via Europa
I-20097 San Donato Milanese, Milan(IT)
Inventor: Crisci, Luciana, Dr.
2, Via Statuto
I-20079 Sant'Angelo Lodigiano,Milan(IT)

(74) Representative: Weinhold, Peter, Dr.
Patentanwälte Dr. V. Schmied-Kowarzik
Dipl.-Ing. G. Dannenberg Dr. P. Weinhold Dr.
D. Gudel Dipl.-Ing. S. Schubert Dr. P. Barz
Siegfriedstrasse 8
W-8000 München 40(DE)

(54) **Stabilizing mixture for compounds having photochromatic activity.**

(57) Described are stabilizing mixtures for photochromatic substances which contain a cyclic amine selected from 1,4-diazabicyclo-[2.2.2]octane, quinuclidine and their derivatives, and at least one sterically hindered amine.

EP 0 476 612 A2

The present invention relates to stabilizing mixtures for compounds having photochromatic activity, which mixtures ensure an exc ptionally long-lasting activity of the corresponding photochromatic compositi ns. The present invention also relates to said photochromatic compositions as well as to articles (products) which are photochromatic due to the presence of said compositions therein.

Photochromatic compounds are substances which are capable of reversibly changing colour and/or the degree of light transmission when exposed to certain types of electromagnetic radiation and solar light, returning again to their initial state of colour and light transmission after the removal of the source of radiation.

There are many known substances which have photochromatic characteristics and which belong to different classes of both organic and inorganic compounds, as described, e.g., in "Photochromism", G.H. Brown (Ed.), Vol.32 of the Weissberger series "Techniques of Organic Chemistry", Wiley Interscience, N.Y. (1971).

Among the relatively well-known organic photochromatic compounds are the spiro-indoline-oxazines and spiro-indoline-pyranes, which compounds can impart photochromatic characteristics to polymer systems for paints, inks and adhesives, as well as to polymerized organic materials used for sun filters, optical instruments, optical memories, printing, photography, fabrics, decorating articles and toys as described, e.g., in US-A-3,562,172, 3,578,602, 4,215,010 and 4,342,668 and in EP-A-134,633 and 141,407.

According to the art, a photochromatic compound can be deposited on an article by means of impregnation or thermal transfer, as specified in US-A-4,286,957.

It also is possible to apply the photochromatic compound dispersed in a paint spread over the surface of the article which is to become photochromatic. These methods of surface application, at times, allow articles to conserve their photochromatic characteristics only for limited periods of time.

The introduction of a photochromatic compound into the mass of an article, especially when the latter is made of thermoplastic material can, on the other hand, create problems to which no satisfactory solution has yet been found. Thermoplastic materials are transformed into finished articles by the usual techniques of moulding, extrusion and the like. Under the conditions (especially of temperature) under which these processes are carried out, the organic photochromatic compounds are likely to undergo degradation or at least degeneration, accompanied by an irreversible development of an undesirable colouring.

In addition, it is also known that organic photochromatic compounds incorporated in polymer matrices or in solutions, undergo rapid degradation, losing their photochromatic activity due to exposure to light under normal conditions of use.

A solution to these problems has been offered by the Applicant through a procedure which, as described in IT-A-21098/88 and 19407/87, comprises the mixing, either before or during the processing phase of the thermoplastic organic polymers, of an organic photochromatic compound with, respectively, a basic organic compound which contains nitrogen, selected from non-cyclic or cyclic non-aromatic amines, amidines and guanidines, or sterically hindered amines containing silicon in their molecule.

There are also known photochromatic compositions (US-A-4,720,356) which are fatigue resistant under light and which include a spirooxazine combined with a sterically hindered amine, selected from those normally used for the stabilization or organic polymers to ultraviolet light.

The stabilization of photochromatic activity imparted by the above-mentioned substances is not ensured, however, for more than a limited, and sometimes not sufficient, period of time, whereafter this activity decreases, even dramatically, making the preparation of photochromatic compositions and corresponding articles and manufactured goods, unreasonably expensive.

It has now surprisingly been found that it is possible to prolong the photochromatic activity of photochromatic substances of interest, beyond any expected limit of the stabilizing effect of the above-mentioned compounds, by adding to one or more of said photochromatic substances a stabilizing mixture comprising (a) at least one cyclic amine selected from 1,4-diazabicyclo-[2.2.2] octane (hereinafter referred to as DABCO), quinuclidine and derivatives of said compounds and (b) at least one sterically hindered amine (hereinafter referred to as HALS). This mixture stabilizes the photochromatic characteristics of the substance to which it has been added for a much longer period than would be expected from the contributions of the individual additives, in such a way that the loss of photochromatic activity occurs after a peri d which is at least sev ral times long r than that observed with a product which does not contain one of the above cyclic amines.

Accordingly the present invention provides a mixture which stabilizes the photochromatic activity of compounds possessing said activity, comprising (a) a cyclic amine selected from 1,4-diazabicyclo-[2.2.2] octane (DABCO), quinuclidine and derivatives thereof and (b) at l ast one st rically hindered amine.

The pres nt invention also provides a fatigue resistant (under light) photochromatic composition with prolonged activity, comprising at l ast one photochromatic compound combined with the above mixture.

In the above composition the weight ratio of mixture of stabilizers to photochromatic compound(s) preferably ranges from 0.5:1 to 50:1, particularly from 2:1 to 25:1, whereas in th abov mixture of stabilizers, th weight ration of cyclic amine (a) to sterically hindered amine (b) usually ranges from 20:1 to 0.5:1, preferably from 10:1 to 1:1.

An additional subject of the present inventi n is a polymeric compositi n which comprises:

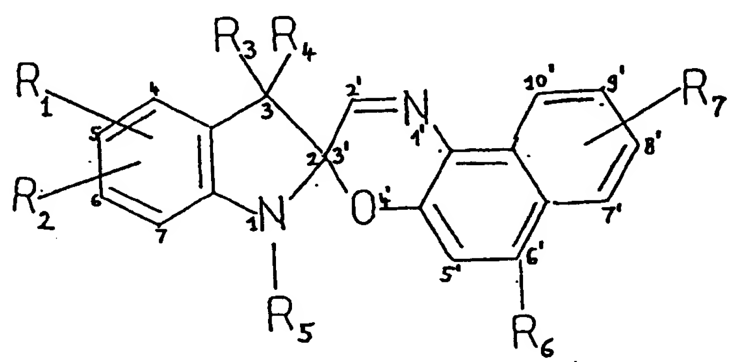
(i) at least one organic polymer;
(ii) at least one photochromatic compound;
(iii) a mixture of stabilizers as defined above;

in which component (ii) is preferably present in amounts of from 0.01 to 3 parts by weight per 100 parts by weight of component (i) and component (iii) is present in the above specified weight ratio with respect to component (ii).

Examples of useful organic polymers are polyolefins such as polyethylene (low and high density as well as linear low density) and polypropylene; polyvinylchloride; plasticized polyvinylchloride; ethylene-vinylacetate (EVA) copolymers; polyvinylacetate; polyvinyl butyral; cellulose acetate; cellulose butyrate; (meth)acrylic resins; polystyrene; polycarbonate; (preferably linear) polyamides and linear polyesters (such as polyethylene terephthalate and polybutylene terephthalate); polyurethanes; and thermosetting polymers derived from poly(allyl carbonates) of polyols.

The stabilizing mixture according to the present invention can be used for any compound having a certain photochromatic activity.

Examples of organic photochromatic compounds which can be used as component (ii) of the above composition are spirooxazines and spiropyranes. Spirooxazines may be represented by the following general formula (A):



(A)

wherein:

R_1 and R_2 independently represent hydrogen, halogen (fluorine, chlorine and bromine) or a group selected from linear or branched C_1-C_5 alkyl or haloalkyl, C_1-C_5 alkoxy, nitro, cyano,carboxyl, carboxyalkyl and carbonyl; R_3 and R_4 independently represent linear or branched C_1-C_5 alkyl, phenyl or benzyl; or R_3 and R_4 together with the carbon atom to which they are bound, form a C_5-C_8 cycloalkyl group; R_5 represents linear or branched C_1-C_5 alkyl, alkylphenyl, benzyl or allyl alkoxy; R_6 represents hydrogen, linear or branched C_1-C_5 alkyl or -NR_8R_9, R_8 being linear or branched C_1-C_5 alkyl, phenyl or benzyl and R_9 being hydrogen or having the same meaning as R_8, or R_8 and R_9, together with the nitrogen atom to which they are linked, forming a cyclic structure with from 5 to 12 members, optionally containing an additional heteroatom selected from oxygen and nitrogen; R_7 represents hydrogen, halogen (fluorine, chlorine or bromine) or a group selected from linear or branched C_1-C_5 alkyl, cyano thioalkyl, ester carboxylate with 1 to 3 carbon atoms in the ester portion, or forms an aromatic or condensed heterocyclic nucleus in one of the positions 7', 8', 9' or 10' with the CH group which can be substituted by N.

In particular, the groups R_1 and R_2, if different from hydrogen, can be connected to any of the positions 4, 5, 6 and 7 of the indolinic part of the molecule. Moreover, the group R_7, when different from hydrogen and an aromatic or condensed h t rocyclic nucleus, can be present in any of the positions 7', 8', 9' and 10' of the naphthenic part of the molecule.

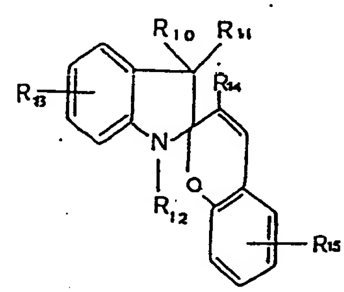
It is preferable t use photochromatic compounds corresponding to general formula (A) in which R_1 and R_2 independently represent hydrog n or methyl; R_3 and R_4 both represent methyl or together with the carbon atom to which they are bound repres nt a cyclohexyl group; R_5 is methyl; R_6 is hydrogen or

$-NR_8R_9$, the groups R_8 and R_9, tog ther with the nitrogen atom to which th y are connected, forming a structure having a piperidine, morpholine, pyrrolidine or hexam thyleneimine nucleus; and R_7 is hydrogen or methoxy.

Examples of preferred photochromatic spirooxazines suitable for the purposes of the present invention are 1,3,3,4,5-and 1,3,3,5,6-pentamethylspiro(indoline-2,3'-(3H)-naphtho(2,1-b)-(1,4)-oxazine); 1,3,3-trimethylspiro(indoline-2,3'-(3H)naphtho-(2,1-b)-(1,4)-oxazine); 1,3,3-trimethylspiro(indoline-6'-(1-piperidine)-2,3-(3H)naphtho-(2,1-b)-(1,4)-oxazine); 1,3,3-trimethylspiro(indoline-6'-(1-morpholine)-2,3'-(3H)-naphtho-(2,1-b)-(1,4)-oxazine); 1,3,3,4,5- and 1,3,3,5,6-pentamethylspiro(indoline-6'-(1-piperidine)-2,3'-(3H)-naphtho-(2,1-b)-1,4)-oxazine); and 1,3,3-trimethylspiro(indoline-6'-(1-piperidine)-9'-(methoxy)-2,3'-(3H)-naphtho(2,1-b)-(1,4)-oxazine).

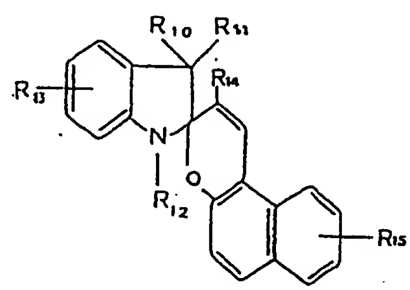
Examples of photochromatic spiropyranes are those represented by the following general formulae (B) to (E):

Indoline spirobenzopyranes



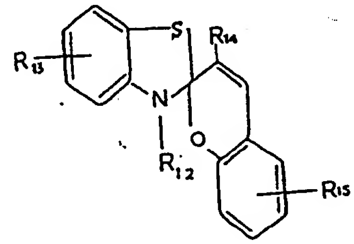
(B)

Indoline spironaphthopyranes



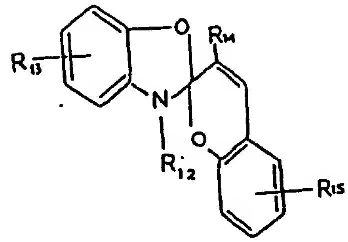
(C)

Benzothiazoline spirobenzopyranes



(D)

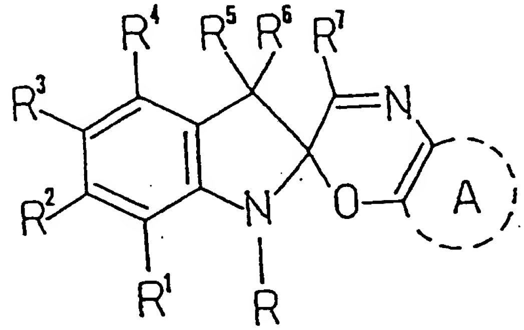
Benzooxazoline spirob nzopyranes



(E)

In the above formulae R_{10} and R_{11} represent alkyl or aryl; R_{12} represents alkyl, aryl, benzyl aryl or substituted alkyl (such as hydroxylalkyl, haloalkyl, carbalkoxyalkyl, alkoxyalkyl, aminoalkyl); R_{14} represents hydrogen, alkyl, aryl or alkoxy; R_{13} and R_{15} represent hydrogen or optionally mono- or polysubstituted alkyl groups, halogen, nitro, alkoxy, cyano, carboxyl, carboxyalkyl and carbonyl.

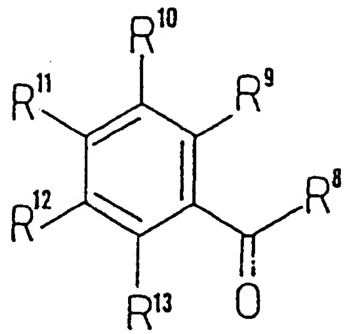
It is also possible to use photochromatic spiro-indolino-oxazines as described in IT-A-22660/89 and defined by general formula (I):



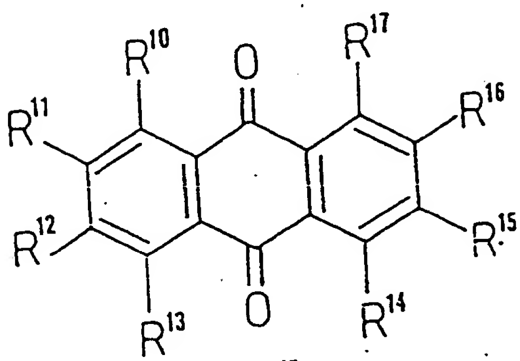
(I)

wherein:

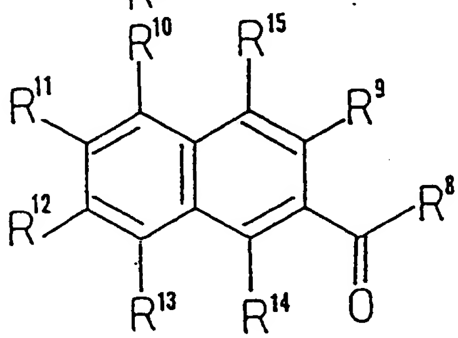
- R represents hydrogen; linear or branched C_1-C_5 alkyl, optionally substituted with from 1 to 5 groups selected from halogen (fluorine, chlorine, bromine and iodine), hydroxy, C_1-C_5 alkoxy, C_1-C_5 carboxyalkyl and cyano; C_2-C_5 alkenyl; phenyl; or benzyl;
- the groups R_1 to R_4, the same or different from each other, represent hydrogen; linear or branched C_1-C_5 alkyl, optionally substituted with from 1 to 5 groups selected from halogen (fluorine, chlorine, bromine and iodine), hydroxy, C_1-C_5 alkoxy, C_1-C_5 carboxyalkyl and cyano; C_2-C_5 alkenyl; benzyl; halogen (fluorine, chlorine, bromine or iodine); hydroxy; C_1-C_5 alkoxy; amino; mono-(C_1-C_5)alkyl amino; di-(C_1-C_5)alkyl amino; (C_3-C_{10})cyclo-alkyl amino; piperidinyl; piperazinyl; morpholyl; carboxyl; carboxy(C_1-C_5)alkyl; carboxy(C_1-C_5)alkenyl; carboxyamido, optionally N-substituted with one or two (C_1-C_5)alkyl groups; cyano; nitro; a sulfonic group; a (C_1-C_5) alkyl sulfonic group; a benzene sulfonic, p-toluene sulfonic or p-chlorotoluene sulfonic group; phenyl; biphenylyl or naphthyl;
- R_5 and R_6, the same or different from each other, represent linear or branched (C_1-C_5) alkyl; phenyl; or R_5 and R_6, together with the carbon atom to which they are connected, represent (C_4-C_7) cycloalkyl;
- R_7 represents hydrogen; linear or branched (C_1-C_5) alkyl; phenyl; halogen (fluorine, chlorine or bromine); (C_1-C_5) alkoxy; or phenoxy;
- A is an arenic, monocyclic or polycyclic group, containing at least one carbonylic function (C=0) on the nucleus or in the side chain, said group being selected from those which can be represented by the following general formulae (II), (III), (IV), (V) and (VI):


R10
R11
R9
R12
R8
R13
O

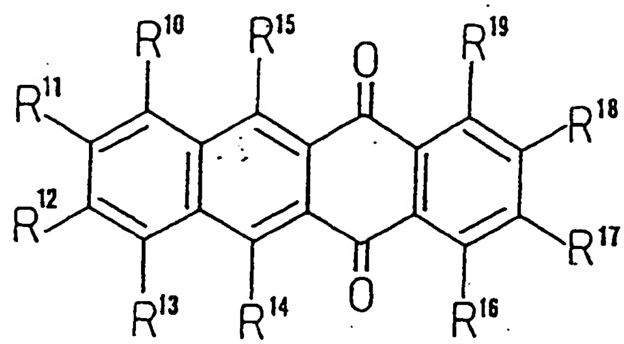
(II)


R10
O
R17
R11
R16
R12
R15
R13
O
R14

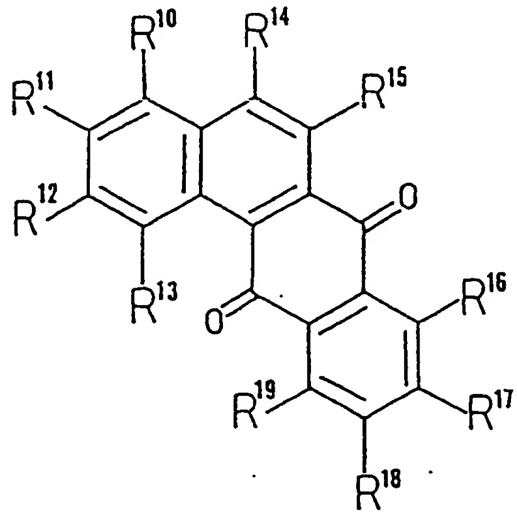
(III)


R10
R15
R11
R9
R12
R8
R13
R14
O

(IV)



(V)



(VI)

wherein:

- R_8 represents hydrogen; chlorine; bromine; linear or branched $(C_1\text{-}C_5)$ alkyl; $(C_2\text{-}C_5)$ alkenyl; and aryl groups selected from phenyl, naphthyl, anthracyl, furanyl, pyrrolyl, thienyl, quinolyl and pyrrolyl, said aryl groups being optionally substituted with from 1 to 4 groups selected from halogen (fluorine, chlorine or bromine), linear or branched $(C_1\text{-}C_5)$ alkyl, hydroxy, $(C_1\text{-}C_5)$ alkoxy, nitro, cyano, amino, mono-$(C_1\text{-}C_5)$alkyl amino, di-$(C_1\text{-}C_5)$alkyl amino, piperidyl, piperazyl or morpholyl;
- two adjacent groups out of R_{10} to R_{13} represent the condensation position with the oxazine nucleus in general formula (I) and the others have the same meaning as the groups R_1 to R_4;
- R_9 and the groups R_{14} to R_{19} have the same meaning as the groups R_1 to R_4.

Preferably, in formula (I):

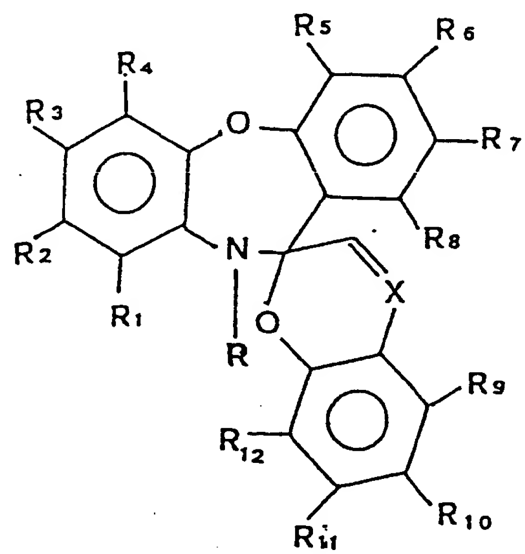
- R represents methyl, ethyl, benzyl, 2-allyl, 2-hydroxyethyl or 2-carboxymethylethyl;
- the groups R_1 to R_4, the same or different from each other, represent hydrogen,fluorine, chlorine, bromine, methyl, isopropyl, trifluoromethyl, hydroxymethyl, benzyl, hydroxy, methoxy, amino, piperidino, morpholino, carboxyl, carboxymethyl, N,N-dimethylcarboxamido, cyano, nitro or phenyl;
- R_5 and R_6, the same or different from each other, represent methyl or phenyl or, together with the carbon atom to which they are connected, represent cyclohexyl;
- R_7 represents hydrogen, chlorine, phenyl, methyl or methoxy;
- A is one of the groups of formulae (II) to (VI) wherein:
- R_8 represents hydrogen, methyl, isopropyl, phenyl, p-N,N-dimethylamino phenyl, p-cyanophenyl, p-nitrophenyl, p-m thoxyphenyl, naphthyl, 2-thienyl, 2-furanyl or 4-pyridyl;
- tw adjacent groups out of R_{10} to R_{13} r present the cond nsation position with the oxazine nucleus in g neral formula (I) and the others each independently represent hydrogen,fluorine, chlorine, bromine, methyl, isopropyl, trifluoromethyl, hydroxymethyl, benzyl, hydroxy, methoxy, amino, piperidino, morpholino, carboxyl, carboxymethyl, N,N-dimethylcarboxamido, cyano, nitro or phenyl;

- R_9 and R_{14} to R_{19} each independently represent hydrogen, fluorine, chlorine, bromine, methyl, isopropyl, trifluor methyl, hydroxymethyl, benzyl, hydroxy, methoxy, amino, piperidino, morpholino, carboxyl, carboxymethyl, N,N-dimethylcarboxamido, cyano, nitro or phenyl.

Specific examples of preferred photochromatic compounds for the purposes of the present invention are:

- 1,3,3-trimethyl-8'-oxyphenyl-spiro-indolino-2,3'-(3H)-naphtho-(2,1-b)-1,4-oxazine (IA);
- 1,1,1-trimethyl-spiro-indolino-2,3'-(3H)-benzo(a)anthracen-7', 12-dione-(3,4-b)-1,4-oxazine (IB); and
- 1,3,3-trimethyl-8'-oxyphenyl-6'-piperidyl-spiro-indolino-2,3'-(3H)-naphtho-(2,1-b)-1,4-oxazine (IC).

It is also possible to use the photochromatic spiro-oxazepin-oxazines described in IT-A-22659/89 and definable by general formula (VII):



(VII)

wherein:

x represents N or CH; R represents hydrogen; linear or branched (C_1-C_5) alkyl, optionally substituted with from 1 to 5 halogen atoms (fluorine, chlorine, bromine or iodine); (C_1-C_5) alkoxy; carboxy (C_1-C_5) alkyl; cyano; (C_2-C_5) alkenyl; phenyl; or benzyl;

the groups R_1 to R_{12}, the same or different from each other, represent hydrogen; linear or branched (C_1-C_5) alkyl; (C_2-C_5) alkenyl; benzyl; halogen (fluorine, chlorine, bromine or iodine); hydroxy; (C_1-C_5) alkoxy; amino; mono-(C_1-C_5) alkyl amino; di-(C_1-C_5) alkyl amino; cyclo-(C_3-C_7) alkyl amino; carboxyl; carboxy-(C_1-C_5) alkyl; carboxamido, optionally N-substituted with one or two (C_1-C_5) alkyl groups; cyano; nitro; or two adjacent groups out of R_9, R_{10}, R_{11} and R_{12} represent a condensed benzenic nucleus which optionally has from 1 to 3 substituents selected from the groups given as meanings for R_1 to R_{12}.

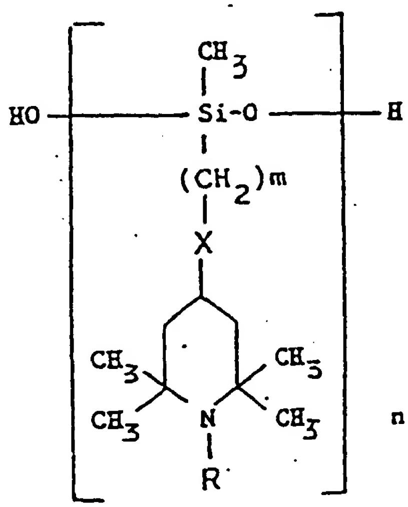
Preferably, in formula (VII) R represents hydrogen or methyl; the groups R_1 to R_8 each independently represent hydrogen or methyl; the groups R_9 to R_{12} each independently represent hydrogen, methoxy or nitro; or two adjacent groups represent a condensed benzenic nucleus without any substituents or carrying from 1 to 3 substituents selected from methoxy, nitro and carboxymethyl.

Specific examples of preferred photochromatic compounds of formula (VII) are:

- 10-methyl-spiro-dibenzo(b,f)-1,4-oxazepin-11,3'-(11h)naphtho-(2,1-b)-(1,4)-oxazine.
- 10-methyl-8'-methoxy-6'-nitro-spiro-dibenzo(b,f)-1,4-oxazepin-11,2'-(11h)benzo(2,1-b)-(3H)pyrane;
- 10-methyl-8'-methoxy-spiro-dibenzo(b,f)-1,4-oxazepin-11,3'-(11h)naphtho(2,1-b)-(1,4)-oxazine; and
- methylic acid ester 10-methyl spiro dibenzo(b,f)-1,4-.

As alr ady mentioned above, the mixture of stabilizing additives according to the pr sent invention contains ne or more cyclic amines sel cted from DABCO, quinuclidine and derivatives of said amines and at least one sterically hindered amine.

One type of suitable sterically hinder d amine can be represented by general formula (VIII):

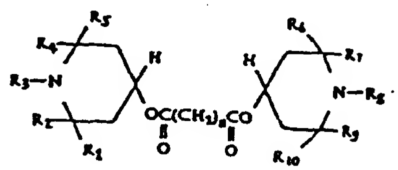


(VIII)

in which R is hydrogen or methyl, X is oxygen or NH, m ranges from 2 to 10 and the average value of n ranges from 1 to 100.

Amines of formula (VIII) are described in IT-A-21935/86.

The stabilizing effect described above can also be obtained by substituting the sterically hindered amine of formula (VIII) with other types of hindered amines; accordingly those corresponding to general formula (IX) may also be used to advantage:

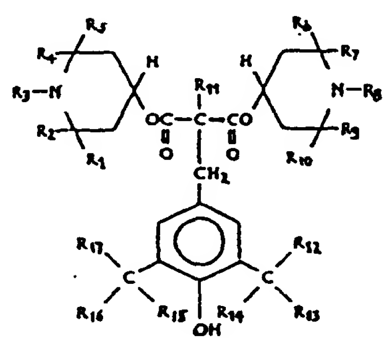


(IX) B-1

in which R_1 to R_{10} independently represent lower alkyl and R_3 and R_8 can additionally be hydrogen; and n ranges from 1 to 12.

(As defined herein, "lower alkyl" is to denote an alkyl group having 1 to 6, preferably 1 to 4 carbon atoms).

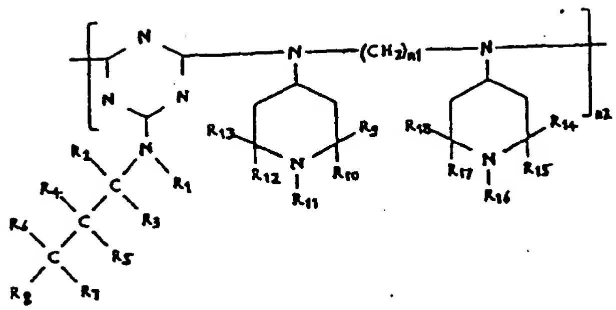
Alternatively, hindered amines of general formula (X) may be used:



(X)

in which R_1 to R_{17} independently represent lower alkyl and R_3 and R_8 can additionally represent hydrogen.

Other suitable hinder d amines ar th se of g n ral formula (XI):

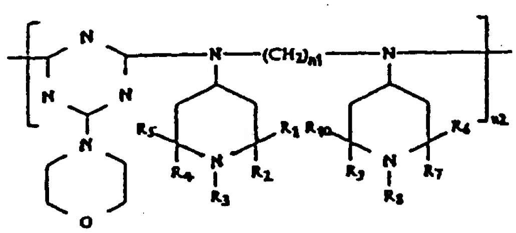


A-1

(XI)

wherein R_1 to R_{18} independently represent lower alkyl and R_1, R_4, R_5, R_{11} and R_{16} can also be hydrogen; n_1 ranges from 1 to 12 and the average value of n_2 is from 1 to 15.

Hindered amines of general formula (XII) can also be used:

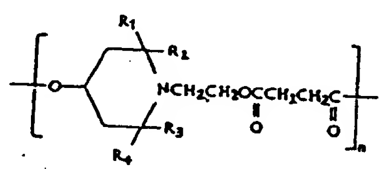


A-1

(XII)

wherein R_1 to R_{10} independently represent lower alkyl and R_3 and R_8 may also be hydrogen; n_1 ranges from 1 to 12 and the average value of n_2 is 1 to 15.

Finally, other suitable hindered amines are those of general formula (XIII):



(XIII)

in which R_1, R_2, R_3 and R_4 independently represent lower alkyl and the average value of n ranges from 1 to 15.

Among the amines of general formula (VIII), it is particularly advantageous to use those in which m is 3 and R represents hydrogen.

Among the amines of general formula (IX), the following specific examples may be mentioned: bis-(2,2,6,6-tetramethyl-4-piperidyl)sebacate (also known as Tinuvin® 770) and bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate (also known as Tinuvin® 765), both being marketed by Ciba-Geigy.

Among the amines of general formula (X), di-(1,2,2,6,6-pentamethyl-4-piperidyl)-butyl-(3',5'-di-tert-butyl-4-hydroxybenzyl)-malonate, better known under the trade-name Tinuvin® 144 (Ciba-Geigy), is of particular int rest.

As far as the compounds f general formula (XI) are concerned, attention is to be directed to the product known as Chimossarb® 924 (Ciba-Geigy), which is poly{[(6-(1,1,3,3-tetram thylbutyl)amine]-1,3,5-triazine-2,4-diyl}-[6-(2,2,6,6-tetramethyl-4-piperidinyl)amino-hexamethylene].

With respect to the amin s of formulae (XI) and (XIII), specific examples thereof are poly[6-(morpholino)-s-triazine-2,4-diyl]-[1,6-(2,2,6,6-tetramethyl-4-piperidyl)amino]hexa methylene, known as Cyasorb® 3346 (American Cyanamide) and Tinuvin® 622 (Ciba-Geigy) which is th dimethylsuccinic ester

of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidylethanol.

The us of compounds of gen ral formulae (VIII) and (XIII) as stabilizers for photochromatic materials has already been described in the above mentioned US-A-4,720,356.

Regarding the fields of application, th photochromatic composition of the present invention can suitably be used for paints, inks, adhesiv s, fibres, fabrics, etc.

More specifically, the photochromatic articles made of plastic, containing the polymeric composition of the present invention (i.e. the mixture of components (i) to (iii)), are obtained by the heat processing of the mixture of the corresponding components; this mixture can be prepared using conventional techniques such as dry mixing, with or without a wetting agent, or by mixing with a volatile solvent and homogenizing with apparatus such as Banbury mixers, calenders, etc.

These mixtures may additionally contain other components, common in the field of thermoplastics, such as inert fillers, plasticizers, pigments, lubricants, antistatic agents, slipping agents, antiblocking agents, etc.

The mixtures of components (i), (ii) and (iii), optionally containing one or more additives (e.g. those already mentioned), may be transformed into finished products by means of heat processing.

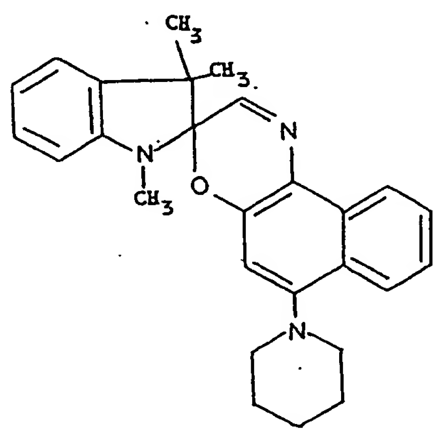
For this purpose, melt processing techniques such as extrusion, spinning, compression moulding, injection moulding, blow moulding, calendering, or reaction injection moulding (RIM), and other techniques which are normally carried out within a temperature range of about 100°C to about 300°C may be used.

In this way, products such as films, fibres, bands, slabs, moulded articles, containers, protective filters, technical articles, transparent sheets of glass, optical instruments, toys and fabrics which show no signs of degradation of the photochromatic compound and which are capable of maintaining their photochromatic characteristics for extremely long periods of time are obtained.

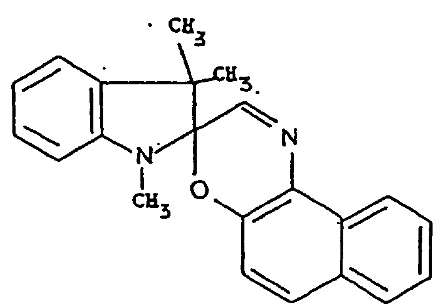
The following examples are to further illustrate the present invention.

In these examples use is made of the following photochromatic compounds (component (ii)):

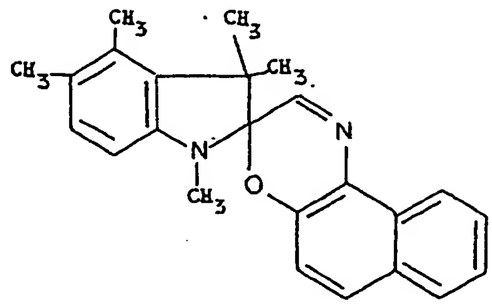
(A) 1,3,3-trimethyl-spiro(indolino-6'-(1-piperidine)-2-3'-(3H)-naphtho-(2,1-b)-(1,4)-oxazine) of formula:



(B) 1,3,3-trimethyl-spiro(indolino-2,3'-(3H)-naphtho-(2,1-b)-(1,4)-oxazine) of formula:

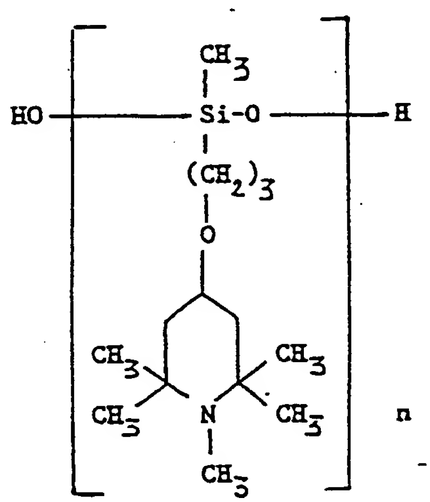


(C) 1,3,3,4,5- and 1,3,3,5,6-pentamethyl-spiro(indolino-2,3'-(3H)-naphtho-(2,1-b)-(1,4)-oxazine) of formula:



and the following sterically hindered amines (second component of the stabilizing mixture (iii)):

HALS 1)



(average value of n about 8)

HALS 2) TINUVIN® 770 (see above).

These components are added to polypropylene and acrylic paint to obtain strips, films and photochromatic prints. The strips and films are obtained by injection moulding or extrusion whereas the paints are applied by screen printing on strips of white cotton and dried in an oven at 110°C for 10 minutes. The following characteristics of the photochromatic products thus obtained are determined:

- UV-visible spectrum, determined with a Cary 2300 spectrophotometer, in absorbance on transparent or translucent materials such as film and polypropylene strips. The optical density measured at the wavelength of maximum absorption of the compound in its deactivated form is considered to be a measure of the concentration of the photochromatic compound in the sample.
- Photochromatic activity estimated by determining the light reflectance variation (ΔR) at 23°C, carried out with a Gardner HAZEMETER XL 211 after activation for 15 seconds with a UV-A lamp having an irradiating power of 9 W/m^2. (For transpar nt materials this measurement is carried out by putting the test samples on white, refl cting cardboard).
- Accelerated aging resistance, as measurement of the duration of the photochromatic activity over a period of time, determined with a Weather-0-M ter (WOM) Atlas equipped with a 6500 W Xenon lamp with continuous irradiation, operating at a temperature of 63°C on a black r ferenc panel and with a relative humidity of 50%. The aging resistance is calculated by measuring,after different times of

exposure to the WOM, the optical density values at λ max of the deactivated form (if possibl) and th r sidual ΔR after activation with a UV-A lamp.

EXAMPLE 1

6 compositions are prepared (Nos. 1-6 in Table 1), composed of Moplen® FLF 20 polypropylene (HIMONT) with a fluidity degree of 11, photochromatic compound A, HALS 1 and 1,4-diazabicyclo-[2.2.2]-octane (DABCO). The amounts of said components are given in parts by weight.

Table 1

Composition No.	1	2	3	4	5	6
FLF 20	100	100	100	100	100	100
Compound A	0.1	0.1	0.1	0.1	0.1	0.1
HALS 1	0.25	-	-	0.25	0.25	0.25
DABCO	-	0.25	2	0.25	0.5	2

Compositions Nos. 1, 2 and 3 are to be considered comparative compositions as only the sterically hindered amine is present in composition No.1, whereas compositions No. 2 and 3 only contain DABCO in two different amounts.

The compositions thus prepared are transformed into 1 mm thick strips, by means of injection moulding at a temperature of 220°C. The optical density (referred to the deactivated form) and photochromatic activity (expressed as ΔR) related to the aging time in the WOM, are shown in Table 2.

Table 2

Aging hours (WOM)	Composition No.	1	2	3	4	5	6
0	(1)	2.479	2.092	2.968	1.854	2.262	2.965
	ΔR	54.3	55.0	54.5	55.8	53.5	53.2
100	(1)	0.821	1.206	2.205	1.413	1.762	2.312
	ΔR	39.1	47.3	51.5	49.5	51.8	52.7
200	(1)	0.000	0.562	1.456	0.936	1.285	1.746
	ΔR	1.5	29.0	42.1	38.7	42.2	43.8

300	(1)	--	0.000	0.753	0.534	0.818	1.320
	ΔR	--	2.5	28.7	20.0	31.8	37.5
400	(1)	--	--	0.168	0.323	0.431	0.84
	ΔR	--	--	5.8	7.0	19.3	33.2

Note: (1) = Optical density of deactivated form (at 360 nm)

The data given in Table 2 clearly show the stabilizing effect of the sterically hindered amine-DABCO mixture, according to the present invention. In particular, a comparison between compositions No. 1, 2 and 4 and between compositions No. 1, 3 and 6, shows that compositions No. 4 and 6, respectively, give better results with respect to aging resistance. Moreover, when compositions No. 4, 5 and 6 in which the quantity of sterically hindered amine is constant whereas the percentage of DABCO increases are compared, it can be seen that by increasing the amount of DABCO, a further improvement in the stability can be obtained.

EXAMPLE 2

Compositions No. 7 and 10 (Table 3) are prepared, composed of acrylic paint with added carboxymethyl cellulose (TEXILAC® 167200 - a commercial product of MONOUKIAN), photochromatic compound B, HALS 2 and DABCO.

Compositions No. 7, 8 and 9 without the stabilizing mixture of the present invention, are used as comparisons. The amounts of components are given in parts by weight.

Table 3

Composition No.	7	8	9	10
TEXILAC®	100	100	100	100
Compound B	1	1	1	1
HALS 2	-	1	-	1
DABCO	-	--	1	1
Toluene	10-15	10-15	10-15	10-15

The paints thus obtained are screen printed on white cotton strips and then dried in an oven at 110°C for 10 minutes. Table 4 below shows the stability results obtained with these paints. In this case aging was determined by measuring the photochromatic activity by means of reflectancy variation measurements (ΔR).

Table 4

Composition No.	7	8	9	10
ΔR *no aging*	28.9	27.1	27.8	28.3
ΔR 20 h WOM	16.5	19.1	23.4	25.4
ΔR 40 h WOM	3.8	9:0	11.8	16.2
ΔR 60 h WOM	0.0	2.2	0.5	8.8

From Table 4 it can be clearly seen that in composition No. 10 the stabilizing effect is much higher than it is in the comparative compositions (Nos. 7, 8 and 9).

EXAMPLE 3

Using the same procedure as in example 2, compositions No. 11 to 14 (Table 5) are prepared using photochromatic compound C, HALS 2 and DABCO. Compositions No. 11, 12 and 13 are used as comparisons.

Table 5

Composition No.	11	12	13	14
TEXILAC®	100	100	100	100
Compound C	1	1	1	1
HALS 2	-	1	-	1
DABCO	-	-	1	1
Toluene	10-15	10-15	10-15	10-15

The above compositions are transformed into prints by screen printing and are evaluated in the same way as in example 2. The results obtained, shown in Table 6 below, demonstrate that composition No. 14 which contains the stabilizing mixture of the present invention, has the best aging resistance.

Table 6

Composition No.	11	12	13	14
ΔR no aging	39.1	40.0	40.5	40.4
ΔR 20 h WOM	30.0	32.2	34.8	36.8
ΔR 40 h WOM	12.1	20.0	18.2	28.2
ΔR 60 h WOM	1.8	4.6	4.2	22.0

Claims

1. Stabilizing mixture for compounds having photochromatic activity, comprising (a) a cyclic amine selected from 1,4-diaza-bicyclo-[2.2.2] octane (DABCO), quinuclidine and derivatives thereof and (b) at least one sterically hindered amine (HALS).

2. Mixture according to claim 1, wherein the weight ratio (a):(b) ranges from 20:1 to 0.5:1, particularly from 10:1 to 1:1.

3. Mixture according to any one of the preceding claims, wherein component (b) is selected from compounds having one of the formulae VIII to XIII as shown in the description and particularly is a compound of formula VIII.

4. Mixture according to any one of the preceding claims, in which the sterically hindered amine is one of formula VIII wherein X is oxygen, m is 3, R is methyl and n has an average value of about 8.

5. Photochromatic composition having a long-lasting activity, containing at least one photochromatic compound and a stabilizing mixture according to any one of claims 1 to 4.

6. Composition according to claim 5, wherein the weight ratio of stabilizing mixture to photochromatic compound(s) ranges from 0.5:1 to 50:1, particularly from 2:1 to 25:1.

7. Composition according to any one of claims 5 and 6, wherein the photochromatic compound is sel cted from thos having on of the formulae (A), (B) and (C) as specifi d in the description,

particularly those having one of the formulae (I) to (VII) as shown in the description.

8. Polymeric composition, comprising one or more organic polymers and a photochromatic composition according to any one of claims 5 to 7.

9. Composition according to claim 8, wherein the photochromatic compound is present in amounts of from 0.01 to 3 parts by weight per 100 parts by weight or organic polymer.

10. Composition according to any one of claims 8 and 9, wherein the organic polymer is selected from polyethylene, polypropylene, polyvinylchloride, plasticized polyvinylchloride, ethylene-vinylacetate copolymers, polyvinylacetate, cellulose acetate, cellulose butyrate, (meth)-acrylic resins, polystyrene, polycarbonate, polyamides, linear polyesters, and mixtures thereof.

11. Manufactured articles, made of polymeric compositions according to any one of claims 8 to 10.